

09/856774  
531 Rec'd PCT. 24 MAY 2001

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<b>UTILITY PATENT APPLICATION TRANSMITTAL</b> (Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))	Attorney Docket No.	S-98/35
	First Inventor or Application Identifier	P. PETROVA ET AL
	Title	FUNCTIONAL TRIFLUOROVINYL ....
	Express Mail Label No.	EE617838231

<b>APPLICATION ELEMENTS</b> See MPEP chapter 600 concerning utility patent application contents.		<b>ADDRESS TO:</b> Assistant Commissioner for Patents Box Patent Application Washington, DC 20231	
1. <input checked="" type="checkbox"/> * Fee Transmittal Form (e.g., PTO/SB/17) (Submit an original and a duplicate for fee processing)	5. <input type="checkbox"/> Microfiche Computer Program (Appendix)		
2. <input checked="" type="checkbox"/> Specification [Total Pages 33] (preferred arrangement set forth below) - Descriptive title of the invention - Cross References to Related Applications - Statement Regarding Fed sponsored R & D - Reference to Microfiche Appendix - Background of the invention - Brief Summary of the invention - Brief Description of the Drawings (if filed) - Detailed Description - Claim(s) - Abstract of the Disclosure	6. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary) a. <input type="checkbox"/> Computer Readable Copy b. <input type="checkbox"/> Paper Copy (identical to computer copy) c. <input type="checkbox"/> Statement verifying identity of above copies		
3. <input type="checkbox"/> Drawing(s) (35 U.S.C. 113) [Total Sheets 0]	<b>ACCOMPANYING APPLICATION PARTS</b>		
4. Oath or Declaration [Total Pages 0] a. <input type="checkbox"/> Newly executed (original or copy) b. <input type="checkbox"/> Copy from a prior application (37 C.F.R. § 1.63(d)) i. <input type="checkbox"/> DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).	7. <input type="checkbox"/> Assignment Papers (cover sheet & document(s)) 8. <input type="checkbox"/> 37 C.F.R. § 3.73(b) Statement <input type="checkbox"/> Power of Attorney (when there is an assignee) 9. <input checked="" type="checkbox"/> English Translation Document (if applicable) 10. <input checked="" type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <input type="checkbox"/> Copies of IDS Citations 11. <input checked="" type="checkbox"/> Preliminary Amendment 12. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) (Should be specifically itemized) 13. <input type="checkbox"/> * Small Entity Statement filed in prior application, Statement(s) <input type="checkbox"/> Status still proper and desired (PTO/SB/09-12) 14. <input type="checkbox"/> Certified Copy of Priority Document(s) (if foreign priority is claimed) 15. <input checked="" type="checkbox"/> Rec- Office Request Form Other: In FR (4) pages 16X English Amendments (1-16) 17X Docs for Prel Admt (1-16) 18X Form PCT/PEA/409 (12) pages		
16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment: <input type="checkbox"/> Continuation <input type="checkbox"/> Divisional <input type="checkbox"/> Continuation-in-part (CIP) of prior application No: _____ / _____ Prior application information: Examiner _____ Group / Art Unit: _____ For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.			
<b>17. CORRESPONDENCE ADDRESS</b>			
<input type="checkbox"/> Customer Number or Bar Code Label <input checked="" type="checkbox"/> Correspondence address below (Insert Customer No. or Attach bar code label here)			
Name	Ashley I. Pezzner, Esquire		
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Name (Print/Type)	ASHLEY I. PEZZNER	Registration No. (Attorney/Agent)	35,646
Signature	<i>Ashley I. Pezzner</i>	Date	05/24/2001-

Burden Hour Statement: This form is estimated to take 0.20 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231.

09/856774

Atty. Docket #: S-98/35

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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INTERNATIONAL APPL. NO.: PCT/EP99/09147 :

INTERNATIONAL FILING DATE: -11/22/1999- :

APPLICANT: PETYA PETROVA ET AL :

SERIAL NO: : ART UNIT:

FILED: -HEREWITH- : EXAMINER:

FOR: "FUNCTIONAL TRIFLUOROVINYL  
MONOMERS  
AND THEIR COPOLYMERIZATION  
WITH FLUOROOLEFINS" :  
:

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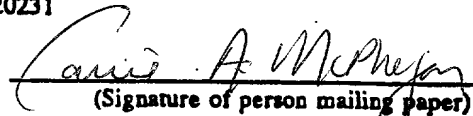
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Box PCT  
Washington, D.C. 20231

"Express Mail" No.: EE617838231

Date: - MAY 24, 2001 -

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

-Carrie A. McPherson-  
(Typed or printed name of mailing paper or fee)

  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS  
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371  
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

09/856774-07401

S-98/35  
09/856774

531 Rec'd PCT 24 MAY 2001

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2)) --
  - a. ☒ is transmitted herewith (required when not transmitted by International Bureau).
  - b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO 00/31009.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A (verified) translation of the International Application into the English language is enclosed.
7. ☒ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☒ are transmitted herewith (required if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
  - e. ☐ will be submitted with the appropriate surcharge.
8. ☒ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)(3)) is enclosed or will be submitted with the appropriate surcharge.

9. ☒ An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) will follow.  
☐ and is attached to the translation of (or a copy of) the International Application.  
☐ and is attached to the substitute specification.

10. ☐ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.  
12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.  
13. ☒ A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.  
14. ☐ A substitute specification (including claims, abstract, drawing) is enclosed.  
15. ☐ A change of power of attorney and/or address letter is enclosed.  
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

☐ 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☒ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

09/856774

531 Rec'd PCT

24 MAY 2001

S-98/35

International Application No. PCT/EP99/09147

- ☒ Receiving Office: EPO
- ☒ IPEA (if filing under 37 CFR 1.495): EPO
- ☒ Priority Claim(s) (35 USC §§ 119, 365):  
FRENCH Appln. 98/14931 filed -November 25, 1998- (11/25/98).
- ☒ A copy of the International Search Report is

☐ enclosed.

☒ attached to the copy of the International  
Application.

- ☒ A copy of the Receiving Office Request Form is enclosed.
- ☒ Form PTO/SB/05 (1) sheet
- ☒ Form PCT/IPEA/409 (12) pages In FR
- ☒ Receiving Office Request Form In FR (4) pages
- ☒ English version of the Amendments under Article 34 (Claims 1-16)

The fee calculation is set forth on the next page of this Transmittal Letter.

09856774-03101

09/856774

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## FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 860.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$80.....<sup>2</sup> -160-

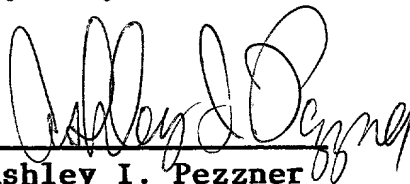
Fee for multiple dependent  
claims \$270..... -0-

TOTAL FILING FEE... \$ 1020.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

Ashley I. Pezzner  
Reg. No. 35,646  
CONNOLLY BOVE LODGE & HUTZ LLP  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

AIP/cam

Enclosures

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(5129\*48)

S-98/35 (5129\*48)  
09/856774

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: PETYA PETROVA *ET AL.* )

531 Rec'd PCT. 24 MAY 2001

SERIAL NO. TO BE ASSIGNED )

ART UNIT: TO BE ASSIGNED

FILED: HEREWITH )

EXAMINER: TO BE ASSIGNED

INTERNATIONAL APPL. NO.: PCT/EP99/09147 )

INTERNATIONAL FILING DATE: 11/22/99 )

FOR: FUNCTIONAL TRIFLUOROVINYL  
MONOMERS AND THEIR  
COPOLYMERIZATION WITH  
FLUOROOLEFINS )

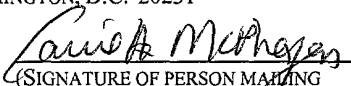
Asst. Commissioner for Patents  
Washington, D.C. 20231

"EXPRESS MAIL" No. EE617838231

DATE: MAY 24, 2001

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON  
(TYPED OR PRINTED NAME OF  
PERSON MAILING PAPER OR FEE)

  
(SIGNATURE OF PERSON MAILING  
PAPER OR FEE)

**PRELIMINARY AMENDMENT**

Sir:

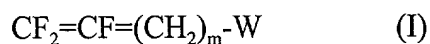
Prior to fee calculation and examination please amend the above-identified application as follows.

**In the Claims**

Please cancel claims 1-19.

Please add the following new claims.

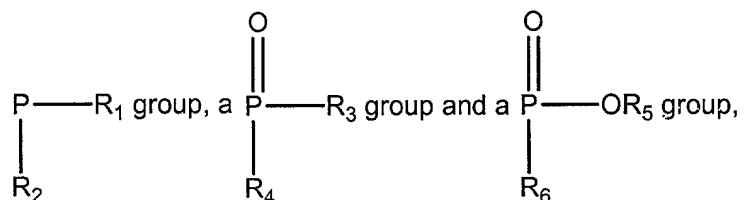
-- 20. A compound corresponding to the formula I



chosen from the compounds in which

(i) m has the value 1, 2 or 3 and

W is selected from the group consisting of



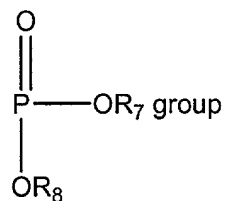
in which

$\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  independently are selected from the group consisting of a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group and an optionally substituted aryl group,

$\text{R}_5$  and  $\text{R}_6$  independently are selected from the group consisting of a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group, with the proviso that, when  $\text{R}_5$  represents a hydrogen atom,  $\text{R}_6$  is other than a phenyl group when m has the value 1;

(ii) m has the value 3 and

W represents a



in which

$\text{R}_7$  and  $\text{R}_8$  independently are selected from the group consisting of a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$



alkyl group and an optionally substituted aryl group;

(iii) m has the value 1 and W represents a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group;

(iv) W represents a Y-Z group chosen from

(1) a Y-Z group in which

Y represents an oxygen atom and

Z is selected from the group consisting of a  $\text{CH}_2\text{CH}_2\text{OH}$  group and a  $\text{CH}_2\text{COOH}$  group and

m has the value 1, 2 or 3

(2) a Y-Z group in which

Y represents an oxygen atom and

Z represents a  $\text{COCH}_3$  group, and

m has the value 1 or 3

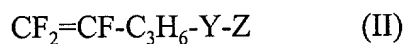
(3) a Y-Z group in which

Y represents a sulphur atom and

Z is selected from the group consisting of a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group and a  $\text{COCH}_3$  group, and

m has the value 3.

21. The compound according to claim 20, wherein the compound of formula I corresponds to the compound of the formula II

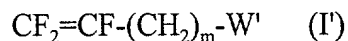


in which Y-Z represents a Y-Z group as defined in claim 20.

22. The compound according to claim 20, wherein the compound of formula I corresponds to the compound of the formula



23. A copolymerization process which comprises reacting a compound corresponding to the formula I'

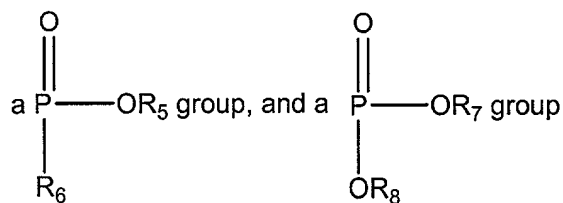
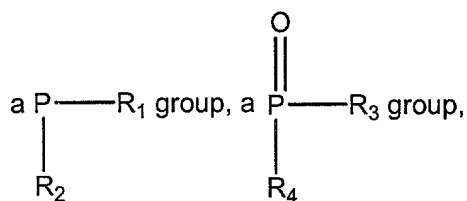


in which

m has the value 1, 2 or 3,

W' is selected from the group consisting of

- (i) W' is selected from the group consisting of a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group, a  $\text{CH}=\text{CH}_2$  group,



in which

$\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$  and  $\text{R}_8$  independently are selected from the group consisting of a

hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group and an optionally substituted aryl group or

- (ii) W' represents a Y-Z group chosen from

a Y-Z group in which

Y represents an oxygen atom and

Z is selected from the group consisting of a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group and

a  $\text{COCH}_3$  group, and

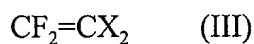
(iii) W' represents a Y-Z group chosen from

a Y-Z group in which

Y represents a sulphur atom and

Z is selected from the group consisting of a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group and a  $\text{COCH}_3$  group,

with a compound corresponding to the formula III

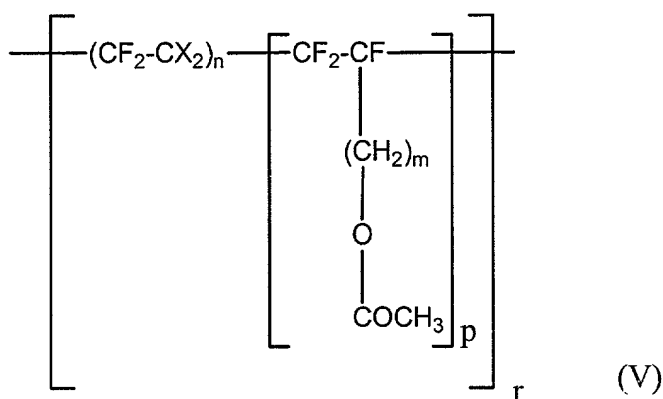


in which

X independently is selected from the group consisting of a hydrogen atom and a fluorine atom,

so as to obtain a fluorocopolymer.

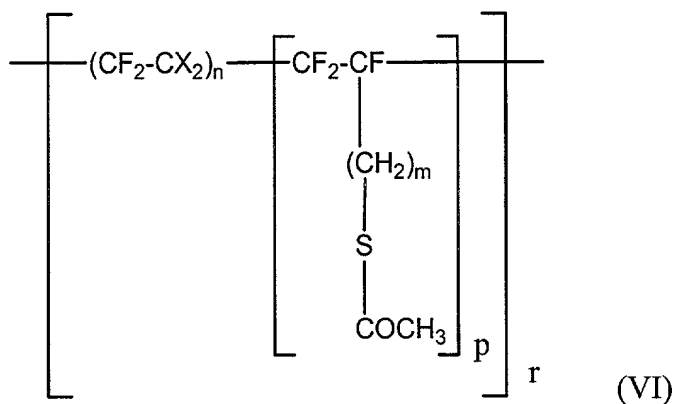
24. The copolymerization process according to claim 23, in which Y represents an oxygen atom, Z represents a  $\text{COCH}_3$  group and the copolymer obtained corresponds to the formula V



wherein n, p and r independently representing natural integers.

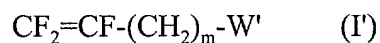
25. The copolymerization process according to claim 23, in which Y represents a sulphur atom,

Z represents a  $\text{COCH}_3$  group and the copolymer obtained corresponds to the formula VI



wherein n, p and r independently representing natural integers.

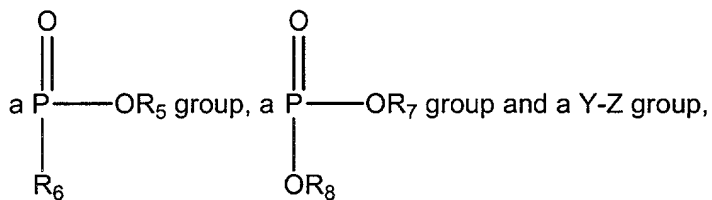
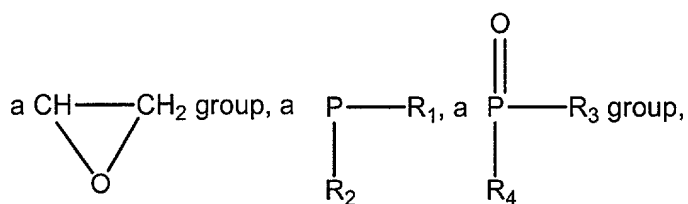
26. A copolymerization process which comprises reacting a compound corresponding to the formula I'



in which

m has the value 1, 2 or 3,

W' is selected from the group consisting of a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group, a  $\text{CH}=\text{CH}_2$  group,



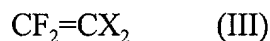
in which

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  independently are selected from the group consisting of a hydrogen atom, a  $C_1$ - $C_{20}$  alkyl group and an optionally substituted aryl group,

$Y$  is selected from the group consisting of an oxygen atom and a sulphur atom and

$Z$  is selected from the group consisting of a hydrogen atom, a  $CH_2CH_2OH$  group, a  $CH_2COOH$  group and a  $COCH_3$  group,

with a compound corresponding to the formula III

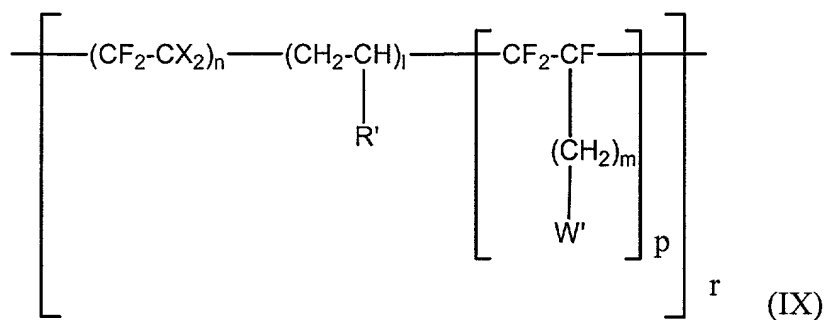


in which

$X$  independently is selected from the group consisting of a hydrogen atom and a fluorine atom,

and with an olefinic compound of formula  $CH_2=CH-R'$  in which  $R'$  is selected from the group consisting of a hydrogen atom and a  $C_1$ - $C_4$  alkyl group,

so as to obtain a copolymer corresponding to the formula IX



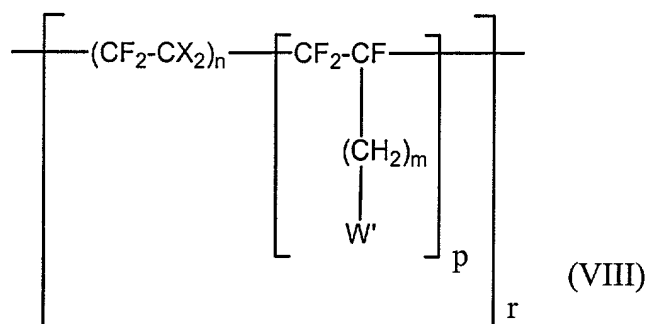
in which

$l, n, p$  and  $r$  independently represent natural integers.

27. The process according to claim 26, wherein  $Z$  is selected from the group consisting of a

CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group and a COCH<sub>3</sub> group.

28. The process according to claim 26, wherein the olefinic compound is propylene.
29. The process according to claim 27, wherein the olefinic compound is propylene.
30. A method for forming fluoroelastomers which comprises using the process according to claim 26.
31. A copolymer corresponding to the formula VIII



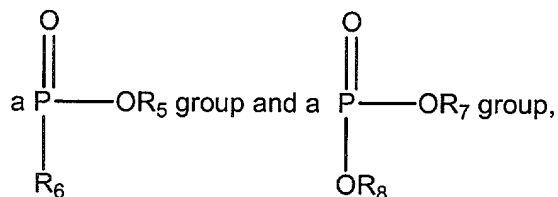
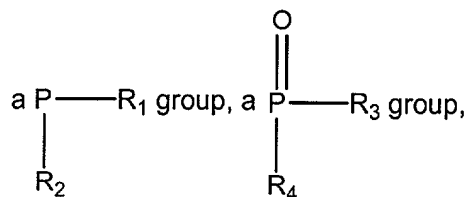
in which

m has the value 1, 2 or 3,

X independently is selected from the group consisting of a hydrogen atom and a fluorine atom,

n, p and r independently represent natural integers, and

W' is selected from the group consisting of a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  independently are selected from the group consisting of a hydrogen atom, a  $C_1$ - $C_{20}$  alkyl group and an optionally substituted aryl group and a Y-Z group chosen from

(1) a Y-Z group in which

Y represents an oxygen atom and

Z is selected from the group consisting of a  $CH_2CH_2OH$  group, a  $CH_2COOH$  group and a  $COCH_3$  group,

(2) a Y-Z group in which

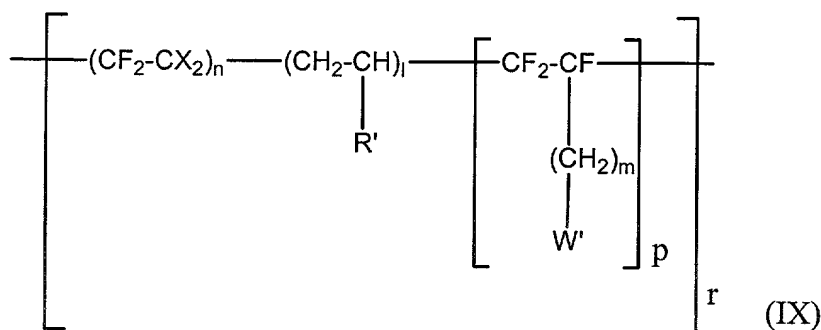
Y represents a sulphur atom and

Z is selected from the group consisting of a hydrogen atom, a  $CH_2CH_2OH$  group, a  $CH_2COOH$  group and a  $COCH_3$  group.

32. The copolymer according to claim 31, in which Y represents an oxygen atom and Z represents a  $COCH_3$  group.

33. The copolymer according to claim 31, in which Y represents a sulphur atom and Z represents a  $COCH_3$  group.

34. A copolymer corresponding to the formula IX



in which

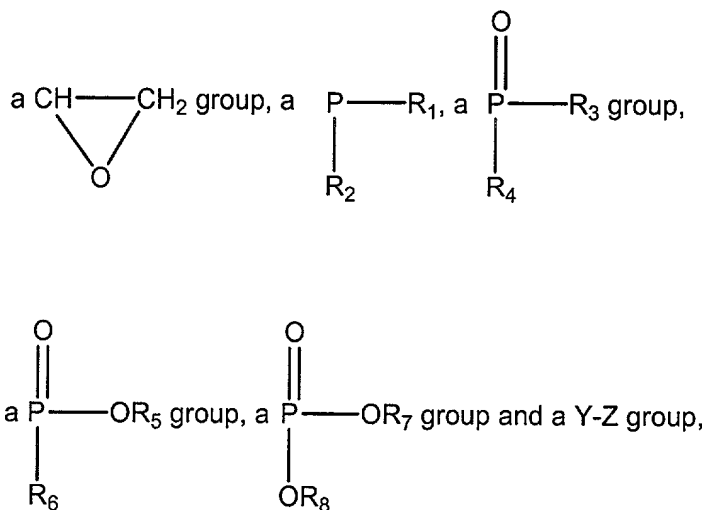
m has the value 1, 2 or 3,

X independently is selected from the group consisting of a hydrogen atom and a fluorine atom,

l, n, p and r independently represent natural integers,

R' is selected from the group consisting of a hydrogen atom and a C<sub>1</sub>-C<sub>4</sub> alkyl group and

W' is selected from the group consisting of a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> independently are selected from the group consisting of a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group and an optionally substituted aryl group,

Y is selected from the group consisting of an oxygen atom and a sulphur atom  
and

Z is selected from the group consisting of a hydrogen atom, a CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group and a COCH<sub>3</sub> group.

35. A crosslinking process comprising the stages of

a) optional deprotection of the functional groups of copolymers according to claim 34,



- b) reaction of the resulting copolymers with an unconjugated C<sub>5</sub>-C<sub>8</sub> diene, so as to obtain crosslinked copolymers.
36. The crosslinking process according to claim 35, wherein said unconjugated diene is 1,5-hexadiene. - -

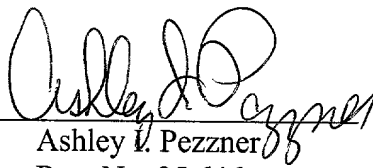
**REMARKS**

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. Support for newly added claims 20-36 can be found in the original 1-19. A fee of \$160.00 is enclosed for the extra 2 independent claims over 3. No additional fee is due. If there are any additional fees due in connection with the filing of this response the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By   
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Functional trifluorovinyl monomers and their  
copolymerization with fluoroolefins

5 The present invention relates to fluoro-  
monomers. It also relates to processes for the  
copolymerization of fluoromonomers with fluoroolefins,  
to the resulting copolymers and to the use of these  
monomers in forming in particular fluoroelastomers. In  
addition, the present invention relates to a process  
10 for the crosslinking of these copolymers.

A large number of fluoromonomers have already  
been disclosed in the literature.

15 The synthesis of fluoroolefins corresponding to  
the general formula  $\text{CF}_2=\text{CF}(\text{CF}_2)_m(\text{CH}_2)_n\text{OH}$  (with  $m = 0$  to  
10 and  $n = 1$  to 4) is disclosed in Patent Application  
EP 0 138 091. The use of fluoroolefins as comonomers of  
vinylidene fluoride is also envisaged.

20 Patent Application EP 0 135 917 discloses  
fluorocopolymers formed by copolymerization of  
vinylidene fluoride with fluoroolefins of general  
formula  $\text{CF}_2=\text{CF}(\text{CF}_2)_m(\text{CH}_2)_n\text{X}$  (with  $\text{X} = \text{OH}$ ,  $\text{COOH}$  or an  
epoxide group,  $m = 0$  to 10 and  $n = 1$  to 4). The  
copolymerization of some of these compounds with  
vinylidene fluoride is described therein.

25 Patent US 3 483 263 discloses the synthesis of  
unsaturated haloalcohols corresponding to the formula  
 $\text{CX}_1\text{X}_2=\text{CX}_3-\text{A}-\text{OH}$  in which  $\text{X}_1$  to  $\text{X}_3$  represent halogen atoms  
and A represents an alkylene group comprising at least  
two carbon atoms.

30 T. Nguyen et al., in J. Organic. Chem., 54(23),  
5640-5642, 1989, disclose the synthesis of a compound  
corresponding to the formula  $\text{CF}_2=\text{CFCH}_2\text{OH}$  by addition of  
methyllithium to 2,2,3,3-tetrafluoropropanol.

35 The document SU 375298 discloses the use of  
 $\text{CF}_2=\text{CFCH}_2\text{OH}$  in the preparation of O-(2,3,3-  
trifluoroalkyl) phosphonates.

The document WO 86/07590 relates to pesticides  
corresponding to the general formula  $\text{CF}_2=\text{CF}-(\text{CH}_2)_n-\text{X}-\text{R}$   
in which X can be O, N, S or  $\text{CH}_2$  and n can have the

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values from 1 to 4, the value of R depending on the meaning of X.

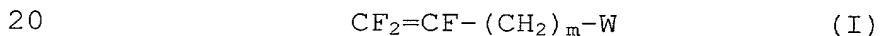
The use of compounds of formula  $\text{CF}_2=\text{CF}-\text{CH}_2\text{Q}$  as pesticides is revealed in United States of America Patent US 5 514 717.

W.R. Dolbier et al., in J. Chem. Soc. Perkin Trans., 2, 219-232, 1998, analysed the cyclization activities of hex-5-enyl radicals and disclosed, inter alia, the synthesis of the compound 4,5,5-trifluoropent-4-enol.

T. Dubuffet et al., in J. Organomet. Chem., 341, 11-18, 1998, reveal a process for the opening of oxetanes under the action of fluorinated organolithium derivatives. Test 13 gives access to the compound 4,5,5-trifluoropent-4-enol.

An object of the present invention consists in making available novel fluoromonomers.

This object is achieved by compounds corresponding to the formula I



in which

m has the value 1, 2 or 3,

W represents a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group, a  $\begin{array}{c} \text{P}-\text{R}_1 \\ | \\ \text{R}_2 \end{array}$  group,

a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{R}_3 \\ | \\ \text{R}_4 \end{array}$  group, a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{OR}_5 \\ | \\ \text{R}_6 \end{array}$  group, a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{OR}_7 \\ | \\ \text{OR}_8 \end{array}$  group or a Y-Z group,

in which

$\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group

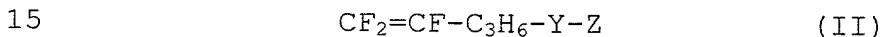
$\text{R}_5$  and  $\text{R}_6$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group, with the proviso that, when  $\text{R}_5$  represents a hydrogen atom,  $\text{R}_6$  is other than a phenyl group when m has the value 1

R<sub>7</sub> and R<sub>8</sub> independently represent a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group or an optionally substituted aryl group, with the proviso that R<sub>7</sub> and R<sub>8</sub> do not both represent a hydrogen atom or an ethyl group when m has the value 1

Y represents an oxygen atom or a sulphur atom and  
Z represents a hydrogen atom, a CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group or a COCH<sub>3</sub> group,

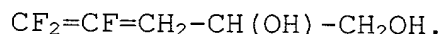
with the proviso that, when W represents CH(OH)CH<sub>2</sub>OH, m has the value 1, when Y represents an oxygen atom, Z is not a hydrogen atom and, when Y represents S, m has the value 3.

More particularly, the present invention provides compounds corresponding to the formula II

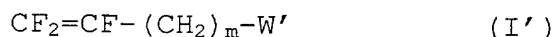


in which Y and Z are as defined above.

Another compound according to the present invention corresponds to the formula



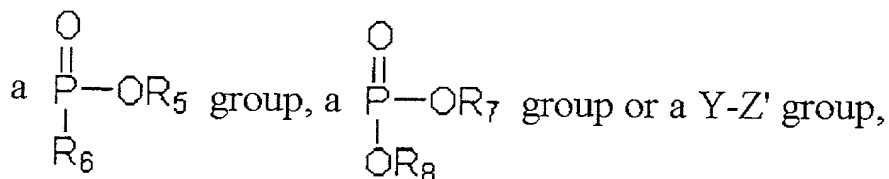
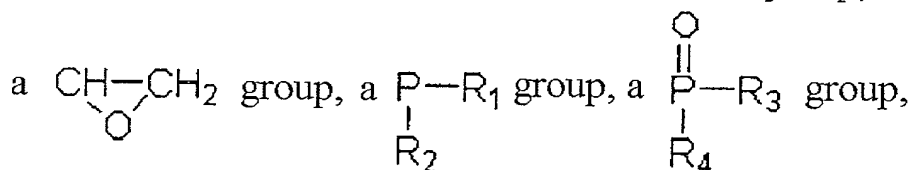
Another object of the present invention is a copolymerization process comprising the reaction of a compound corresponding to the formula I'



in which

m has the value 1, 2 or 3,

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> independently represent a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and  
Z' represents a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  
 $\text{CH}_2\text{COOH}$  group or a  $\text{COCH}_3$  group,

with a compound corresponding to the formula III



in which

X independently represents a hydrogen atom or a  
fluorine atom

with the proviso that, when m has the value 1 and X

represents a hydrogen atom, W' does not represent a  
 $\text{CH}-\text{CH}_2$  group,  
 $\text{O}$

so as to obtain a fluorocopolymer.

One embodiment of the present invention is a  
copolymerization process comprising the reaction of a  
compound corresponding to the formula I'

in which

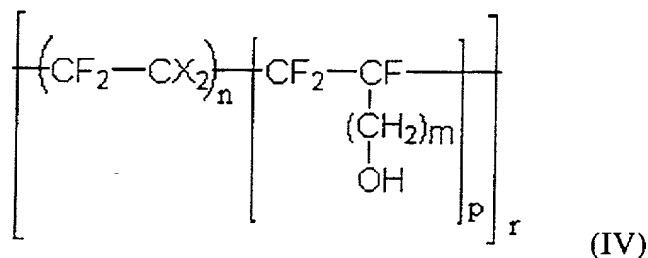
m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom  
and Z' represents a hydrogen atom

with a compound corresponding to the formula III

in which X independently represents a hydrogen atom or  
a fluorine atom

so as to obtain a copolymer corresponding to the  
formula IV



n, p and r independently representing natural integers.

An additional aspect of the present invention  
is a copolymerization process comprising the reaction  
of a compound corresponding to the formula I'

in which

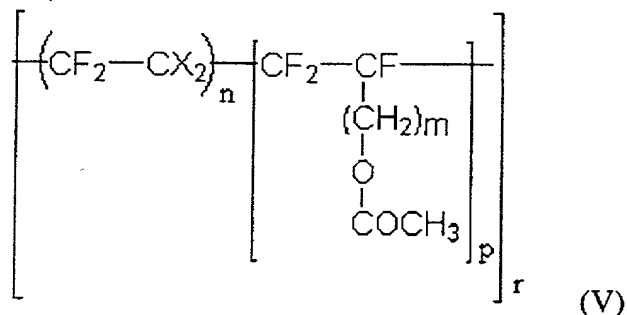
m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom  
and Z' represents a  $\text{COCH}_3$  group

with a compound corresponding to the formula III

in which X independently represents a hydrogen atom or a fluorine atom

so as to obtain a copolymer corresponding to the formula V



n, p and r independently representing natural integers.

The present invention also envisages a copolymerization process comprising the reaction of a compound corresponding to the formula I'

in which

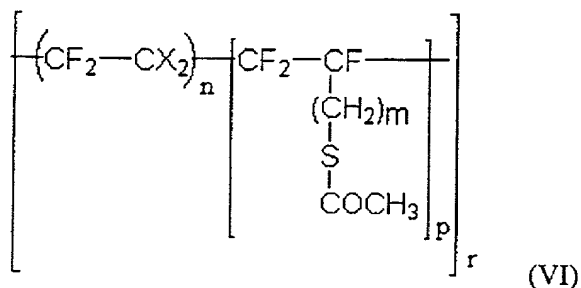
m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents a sulphur atom and Z' represents a COCH<sub>3</sub> group

with a compound corresponding to the formula III

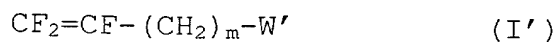
in which X independently represents a hydrogen atom or a fluorine atom

so as to obtain a copolymer corresponding to the formula VI



n, p and r independently representing natural integers.

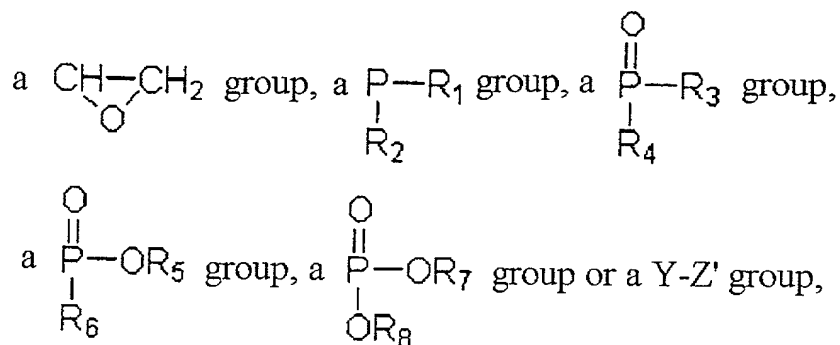
According to yet another preferred embodiment, a copolymerization process is provided comprising the reaction of a compound corresponding to the formula I'



in which

m has the value 1, 2 or 3,

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> independently represent  
 5 a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group or  
 an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH<sub>2</sub>CH<sub>2</sub>OH group, a  
 CH<sub>2</sub>COOH group or a COCH<sub>3</sub> group,

10 with a compound corresponding to the formula III



in which

X independently represents a hydrogen atom or a  
 fluorine atom

15 and with an olefinic compound  
 so as to obtain a copolymer.

More particularly, the invention relates to a  
 copolymerization process comprising the reaction of a  
 compound corresponding to the formula I'

20 in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom  
 and Z' represents a hydrogen atom

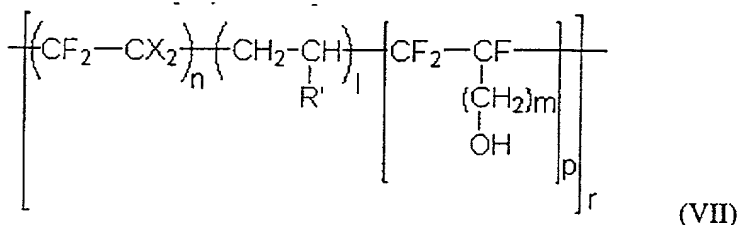
with a compound corresponding to the formula III

25 in which X independently represents a hydrogen atom or  
 a fluorine atom

and with an olefinic compound of formula CH<sub>2</sub>=CHR' with  
 R' representing a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group  
 so as to obtain a copolymer corresponding to the

30 formula VII

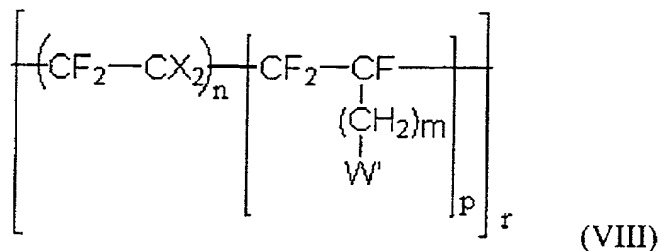
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l, n, p and r independently representing natural integers. Examples of C<sub>1</sub>-C<sub>4</sub> alkyl groups are ethylene, propylene and butylene.

5 Fluoropolymers possess outstanding properties, such as their hydro- and oleophobicity, their thermal stability, their chemical inertia to acids, to bases, to solvents and to hydrocarbons, their resistance to ageing and to UV radiation and their low surface  
10 tension. They find highly varied applications, often in high-tech industries, such as microelectronics, the chemical industry, the automobile industry, the petroleum industry and the aeronautics industry. However, the high melting and glass transition  
15 temperatures of most of these polymers prove to be a limitation on their use which thus requires a significant energy input.

In order to limit this disadvantage, the present invention provides, according to another of its  
20 aspects, copolymers corresponding to the general formula VIII



in which

m has the value 1, 2 or 3,

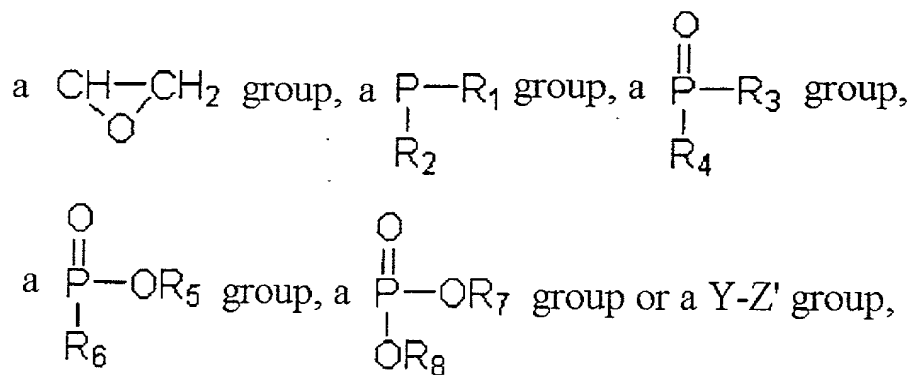
25 X independently represents a hydrogen atom or a fluorine atom,

n, p and r independently represent natural integers, and

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,

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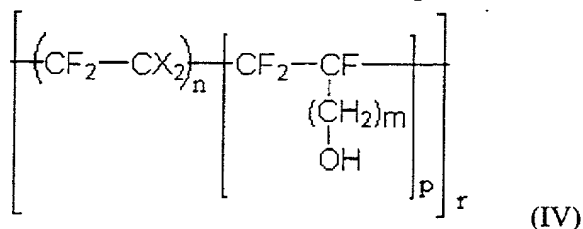
in which

$\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{R}_6, \text{R}_7$  and  $\text{R}_8$  independently represent  
a hydrogen atom, a  $\text{C}_1\text{-C}_{20}$  alkyl group or  
an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  
 $\text{CH}_2\text{COOH}$  group or a  $\text{COCH}_3$  group.

More specifically, the present invention  
relates to copolymers corresponding to the formula IV



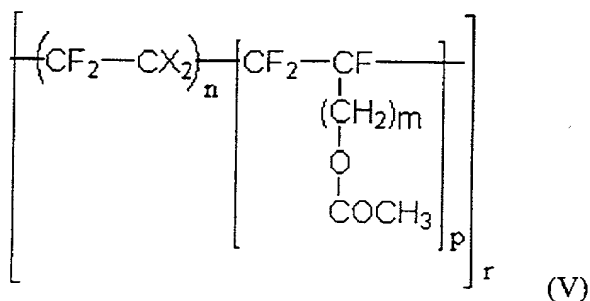
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a  
fluorine atom and

n, p and r independently represent natural integers.

The present invention also relates to  
copolymers corresponding to the formula V



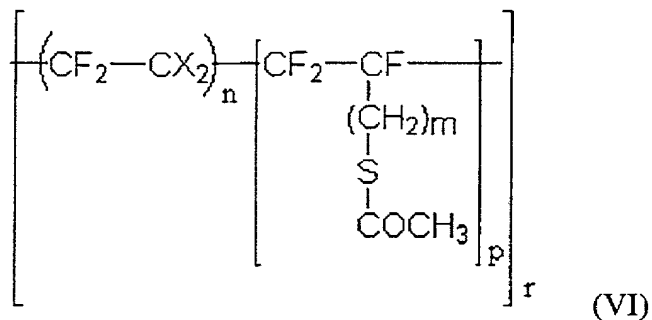
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom and

n, p and r independently represent natural integers.

The present invention also relates to  
5 copolymers corresponding to the formula VI



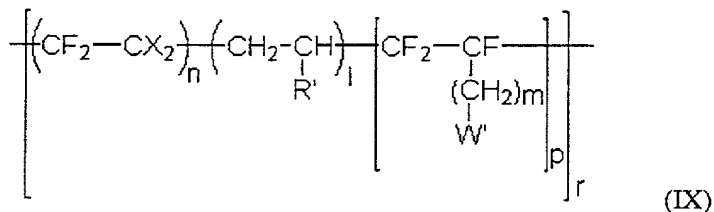
in which

m has the value 1, 2 or 3,

10 X independently represents a hydrogen atom or a fluorine atom and

n, p and r independently represent natural integers.

Other copolymers provided by the present invention are copolymers corresponding to the general formula IX



15 in which

m has the value 1, 2 or 3,

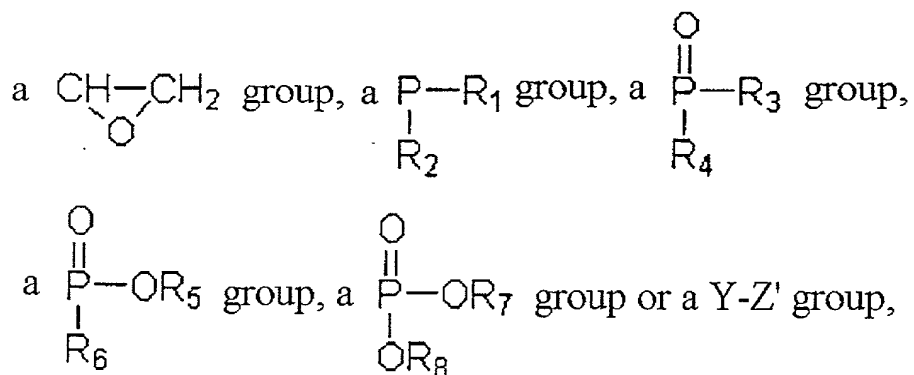
X independently represents a hydrogen atom or a fluorine atom,

20 l, n, p and r independently represent natural integers,

R' represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group and

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,

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in which

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  independently represent  
a hydrogen atom, a  $C_1$ - $C_{20}$  alkyl group or  
an optionally substituted aryl group

$Y$  represents an oxygen atom or a sulphur atom and

$Z'$  represents a hydrogen atom, a  $CH_2CH_2OH$  group, a  
 $CH_2COOH$  group or a  $COCH_3$  group.

More specifically, the present invention  
provides copolymers corresponding to the formula IX,  
in which

$m$  has the value 1, 2 or 3,

$X$  independently represents a hydrogen atom or a  
fluorine atom,

$W'$  represents  $Y-Z'$  and  $Y$  represents an oxygen atom  
and  $Z'$  represents a hydrogen atom

$l, n, p$  and  $r$  independently represent natural integers  
and  $R'$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl  
group.

These copolymers comprise monomers exhibiting  
the  $CF_2=CF-R''-W'$  structure,  $R''$  denoting a spacer arm of  
variable length targeted at introducing free volumes  
and at thus reducing the melting and glass transition  
temperatures.

In order to further improve the properties  
(particularly mechanical properties) of these  
fluoro(co)polymers, it is often desirable to crosslink  
them but this crosslinking to date has required the use  
of nucleophilic agents (such as diamines or bisphenols)  
or of radical systems (triallyl cyanurate radicals) or  
electron bombardment. Consequently, with the aim of

avoiding this additional stage, which constitutes a fairly complex procedure, the present invention provides for the incorporation of crosslinking sites (W' functional group in the above fluoromonomers) directly in the (co)polymers.

An additional object of the present invention is a crosslinking process comprising the stages of

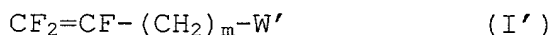
a) optional deprotection of the functional groups of copolymers obtained above,

b) reaction of the resulting copolymers with an unconjugated C<sub>5</sub>-C<sub>8</sub> diene,

so as to obtain crosslinked copolymers.

Examples of unconjugated dienes are 1,4-pentadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene. The use of 1,5-hexadiene as unconjugated diene is particularly preferred.

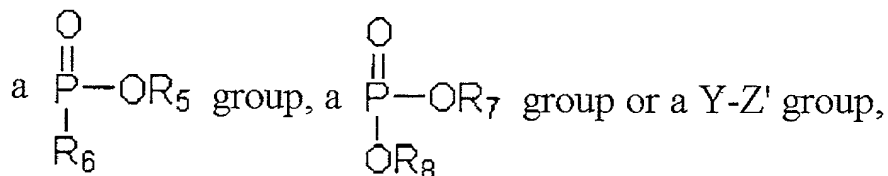
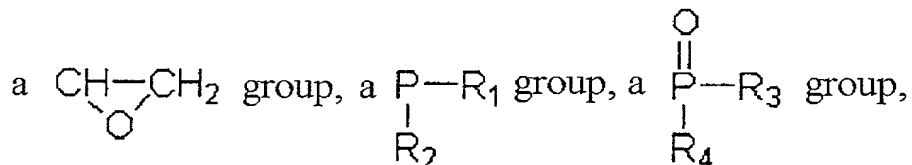
Finally, the use is also provided of compounds corresponding to the formula I'



in which

m has the value 1, 2 or 3,

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> independently represent a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group or a COCH<sub>3</sub> group,

with a compound corresponding to the formula III



in which X independently represents a hydrogen atom or a fluorine atom, preferably a hydrogen atom and optionally with an olefinic compound, to form  
5 fluoroelastomers. Examples of olefinic compounds are ethylene, propylene and butylene. The olefinic compound is preferably propylene.

The invention is described in more detail, without implied limitation, in the following examples.

10 Example 1

Preparation of  $\text{CF}_2=\text{CFCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$

- a) Radical addition of iododichlorotrifluoroethane to allyl acetate

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15 A mixture composed of 292.2 g (1.050 mol) of iododichlorotrifluoroethane and of 106.5 g (1.065 mol) of allyl acetate was heated with stirring to 55°C in a three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. 1.4 g (3.5 mmol) of t-butyl  
20 cyclohexyl peroxycarbonate were added at this temperature and, after 30 minutes, the addition of an equivalent amount of initiator results in an increase in the temperature of the reaction medium to 70°C. After 30 minutes, an additional 1.4 g of  
25 initiator were injected into the mixture and brought about a strong exothermic reaction to 175°C (over 10 seconds) which rendered the crude product colourless, followed by a dark brown mixture. After evaporating the unreacted iodo-  
30 dichlorotrifluoroethane and allyl acetate, the product mixture was distilled. Boiling point = 101-105°C/0.2 mmHg (lit. val.: 113°C/2 mmHg or 107-110°C/0.5 mmHg). 236.8 g (0.63 mol) of a dark liquid were obtained  
35 (yield = 60%).

- b) Epoxidation

9.0 g (0.16 mol) of potassium hydroxide were introduced into 40 g of hexane in a three-necked round-bottomed flask equipped with a reflux

condenser and a mechanical stirrer. 30.5 g (0.08 mol) of the product resulting from the preceding stage were added dropwise to the mixture at ambient temperature. After completing the addition, the medium was heated to 70°C with stirring. After cooling, the KI precipitate was removed by filtration and the crude product was distilled. 11.95 g (0.057 mol) of a light brown liquid were obtained, boiling point = 53-55°C/23 mmHg (yield = 72%).

4,5-Dichloro-4,5,5-trifluoro-1,2-epoxypentane was produced in a proportion of 95.1%, whereas 5,5-dichloro-4,4,5-trifluoro-1,2-epoxypentane was obtained in a proportion of 4.9%.

c) Synthesis of halogenated 1,2-diol by opening of the epoxide ring

A mixture composed of 5.0 g (23.8 mmol) of 4,5-dichloro-4,5,5-trifluoro-1,2-epoxypentane, 11 ml of demineralized water, 11 ml of dioxane and 4 drops of 12N sulphuric acid was stirred in a single-necked round-bottomed flask equipped with a reflux condenser. The medium was heated at reflux for 12 hours. After the reaction, the dioxane was distilled off and the 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane was extracted with diethyl ether, dried over sodium sulphate and distilled. Boiling point = 28-30°C/26 mmHg. 4.01 g (17.7 mmol) of a colourless liquid were obtained. Yield = 75% of 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane.

d) Dechlorination of the 1,2-diol

A mixture of 2.37 g (0.036 mol) of activated zinc in 25 ml of dry DMF was stirred in a two-necked round-bottomed flask purged with argon and equipped with a reflux condenser. The temperature of the medium was increased to 70°C and 3.75 g (16.5 mmol) of 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane obtained above were added dropwise. After reacting for 16 hours, the crude

product was cooled to ambient temperature and the unreacted zinc was removed by filtration. The filtrate was treated with 10% HCl and the product was extracted with 1,2,2-trifluoro-1,1,2-trichloroethane. After distilling off the solvent, the  $\text{CF}_2=\text{CFCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$  was rectified in the form of a colourless liquid (0.88 g, 5.6 mmol, yield = 34%), boiling point = 106-110°C.

Example 2

10 Preparation of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{COOH}$

a) Photochemical initiation (excess of diene)

0906774-073401  
15 A Carius tube comprising 0.055 g (0.3 mmol) of benzophenone, 1.84 g (20 mmol) of thioglycolic acid, 5.00 g (41 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 9.0 g of acetonitrile was cooled in an acetone/liquid nitrogen mixture and degassed under vacuum with 5 freezing/thawing cycles, so as to remove the oxygen. It was subsequently sealed and irradiated under a UV lamp  
20 for 16 hours. After the reaction, the tube was frozen in liquid nitrogen and opened, and the solvent and the volatile fractions were evaporated under vacuum (0.01 mmHg). 1,1,2-Trifluoro-6-thiaocten-8-oic acid was distilled first to give  
25 1.9 g of a pale yellow liquid. Boiling point = 87-90°C/0.15 mmHg (yield = 44%).

b) Photochemical initiation (threefold excess of thioglycolic acid)

30 A similar test to that indicated above was carried out in the presence of 0.083 g (0.46 mmol) of benzophenone, 8.42 g (91.5 mmol) of thioglycolic acid, 3.72 g (30.5 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 10.0 g of acetonitrile. After the same treatment and after the distillation of  
35 the excess thioglycolic acid, 5.29 g of a yellow wax were obtained (yield = 81%), 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic acid..

c) Radical initiation in the presence of azobisisobutyronitrile (AIBN)

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A stirred mixture composed of 0.049 g (0.3 mmol) of AIBN, 1.5 g (16.3 mmol) of thioglycolic acid, 1.99 g (16.3 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 10 g of acetonitrile was heated at 80°C for 7 hours in a sealed Carius tube. After the reaction and the opening of the tube, the solvent and the unreacted starting materials were evaporated. The brown residue was eluted by flash chromatography on a silica bed with diethyl ether, so as to give an orange oil. The overall yield was 46%. In accordance with the integration of the characteristic signals of the  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra, the yields of 1,1,2-trifluoro-6-thiaocten-8-oic acid, of 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic acid and of 4,5,5-trifluoro-6-thiaoctan-8-oic acid were 26, 37 and 37% respectively.

A similar experiment, initiated by t-butyl cyclohexyl peroxy carbonate, at 60°C for 5 hours gave 68% of 1,1,2-trifluoro-6-thiaocten-8-oic acid, 7% of 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic acid and 25% of 4,5,5-trifluoro-6-thiaoctan-8-oic acid with an overall yield of 67%.

d) Radical initiation in the presence of di-t-butyl peroxide

Under similar conditions to those described above, 500 g (0.04 mol) of 1,1,2-trifluoro-1,4-pentadiene, 3.80 g (0.04 mol) of thioglycolic acid, 0.117 g (0.8 mmol) of di-t-butyl peroxide and 10 ml of acetonitrile were reacted. After stirring at 140°C for 6 h and after opening the tube, the solvent was evaporated and the residue was dried at 55°C under 0.1 mmHg to constant weight. A viscous brown liquid was obtained (4.3 g) which is insoluble in chloroform, acetone, DMF, dimethylacetamide, THF and 1,2,2-trifluoroethane. The yield was 49% by mass.



Example 3

Preparation of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$

The reaction was carried out in a Carius tube comprising a stirred mixture composed of 0.19 g (1.0 mmol) of benzophenone, 2.70 g (34 mmol) of 2-mercaptoethanol, 5.01 g (41 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 9.5 g of acetonitrile. After 6 freezing/thawing cycles, the tube was exposed to UV light at ambient temperature (approximately 25°C) for 14 hours. After a similar treatment, the crude product was purified and the  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$  was distilled. 2.03 g of a colourless liquid were obtained (yield = 29%); boiling point 65-66°C/1 mmHg, 1,1,2-trifluoro-6-thiaoctanol.

Example 4

Preparation of  $\text{CF}_2\text{CFCH}_2\text{OH}$

12.4 g (94 mmol) of 2,2,3,3-tetrafluoropropanol, 62.5 ml (367 mmol) of anhydrous dibutyl ether and 9.5 g (94 mmol) of diisopropylamine were placed in a three-necked round-bottomed flask, dried under vacuum and purged with argon so as to remove moisture, equipped with a reflux condenser, a thermometer and a dropping funnel. The mixture was cooled to approximately 0°C. Subsequently, 100 ml (200 mmol) of a 2M solution of butyllithium in pentane were added dropwise for 30 minutes, so as to prevent the temperature from exceeding 5°C. After stirring for 1 hour, the medium was cooled to -50°C in an acetone/liquid nitrogen bath. The excess butyllithium was decomposed using a solution of concentrated sulphuric acid (9.4 ml in 30 ml of water) and the mixture was reheated to ambient temperature. The organic phase was separated by successive rinsings with a saturated sodium hydrogencarbonate solution and with water and then dried over anhydrous  $\text{MgSO}_4$ . Subsequently, the products were rectified at atmospheric pressure, so as to separate the pentane (boiling point 35°C), 32 mmol of 2,3,3-trifluoroallyl alcohol (boiling point 98°C) and the dibutyl ether

(143°C). Even after a second rectification, dibutyl ether was still present in the fluoroalcohol fraction and the yield obtained by  $^1\text{H}$  and  $^{19}\text{F}$  NMR was 34%.

Example 5

5 Preparation of  $\text{CF}_2=\text{CFC}_3\text{H}_6\text{OH}$

a) Radical addition of 1-iodo-1,2-dichlorotrifluoroethane to allyl alcohol

1) Reaction at atmospheric pressure

10 A mixture composed of 171.1 g (0.617 mol) of  $\text{Cl}(\text{C}_2\text{F}_3\text{Cl})\text{I}$  and 98.3 g (1.69 mol) of allyl alcohol was stirred in a three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. The mixture was heated to 80°C and 2.30 g (0.014 mol) of AIBN were added thereto every hour. The reaction was monitored by gas phase chromatography (GC) until the iodinated reactant had been virtually completely consumed. Subsequently, the 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol was distilled. 167.5 g (0.497 mol) of an orange-yellow liquid were obtained. Yield = 81%. Boiling point = 64-66°C/0.2 mmHg. 2-Iodo-4,5,5-trifluoro-4,5-dichloropentanol.

2) Reaction carried out in a Carius tube

25 A Carius tube saturated with nitrogen was filled with 40.0 g (0.14 mol) of  $\text{Cl}(\text{C}_2\text{F}_3\text{Cl})\text{I}$ , with 17.1 g (0.28 mol) of allyl alcohol and with 0.92 g (0.014 mol) of copper powder. The tube was degassed by 5 freezing/thawing cycles and subsequently sealed. It was introduced into an oven incorporating agitation and heated at 120°C for 7 h. After the reaction and cooling to ambient temperature, the tube was frozen in liquid nitrogen and subsequently opened. Once ambient temperature was reached, the crude product was diluted in diethyl ether and the copper was removed by filtration. After an acid treatment, neutralization and evaporation of the solvent, the crude product was analysed by

GC. The yield was estimated at 62%, 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol.

b) Reduction of 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol

5 80.0 g (0.27 mol) of tributyltin hydride were added dropwise with stirring to 88.9 g (0.26 mol) of 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol placed in a flask, saturated with argon and equipped with a septum, cooled in an ice bath. The addition took 30 minutes, the ice bath having been gradually reduced. The mixture was then stirred for an additional 3 hours at ambient temperature. Subsequently, the reduced derivative, 4,5-dichloro-4,5,5-trifluoropentanol, was

10 distilled under reduced pressure. 47.2 g (0.225 mol) of a light yellow liquid were obtained (yield = 86.5%). Boiling point = 80-82°C/23 mmHg.

15

c) Dechlorination of 4,5-dichloro-4,5,5-trifluoropentanol

20 100 ml of dry DMF were introduced, via a septum, into a three-necked round-bottomed flask rinsed with a flow of argon and equipped with a reflux condenser. 46.8 g (0.72 mol) of zinc activated by 5 cm<sup>3</sup> of acetic acid and 5 cm<sup>3</sup> of acetic anhydride were introduced, with vigorous stirring, into the flask and the suspension was heated to 90°C. Subsequently, 50.0 g (0.237 mol) of 4,5-dichloro-4,5,5-trifluoropentanol were added dropwise and the temperature was maintained at 90°C for 4 hours after the completion of the addition. The reaction was monitored by GC, the respective retention times for the trifluorovinyl and chlorinated alcohols being 2.75 and 5.04 minutes respectively. After cooling, the excess zinc was removed by

25 filtration and the crude product was treated with 10% HCl and the fluorinated fraction was extracted with diethyl ether. After distilling off the solvent, the 4,5,5-trifluoropent-4-en-1-ol was rectified. 23.3 g (0.166 mol) of a colourless

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liquid were obtained. Boiling point = 53-55°C/24 mmHg (lit. val.: 95°C/155 mmHg). Yield = 70%.

Example 6

5 Preparation of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{OCOCH}_3$

31.7 g (0.41 mol) of acetyl chloride were added dropwise to a two-necked round-bottomed flask, cooled in an ice bath, equipped with a reflux condenser (connected to a trap comprising potassium carbonate) and comprising 50.1 g (0.36 mol) of 4,5,5-trifluoropent-4-en-1-ol. The reactivity of the two reactants was monitored by sparging of the trap by HCl. After the completion of the addition, the mixture was stirred at ambient temperature until HCl was no longer being evolved (approximately 4 hours). After distillation, 59.3 g (0.326 mol) of 4,5,5-trifluoro-4-pentenyl acetate (colourless liquid) were obtained. Boiling point = 56-58°C/21 mmHg. (Yield = 91%),

Example 7

20 Copolymerization of trifluorovinyl alcohols with tetrafluoroethylene (TFE)

a) 2,3,3-Trifluoroallyl alcohol (FA1)

The copolymerization in solution (in 34% by weight of butyl ether) of TFE with 2,3,3-trifluoroallyl alcohol was carried out by a batchwise process in 30 and 50 cm<sup>3</sup> stainless steel autoclaves equipped with a magnetic stirrer, a safety valve, an accurate manometer ( $\pm 0.01$  MPa) and a thermometer ( $\pm 0.2^\circ\text{C}$ ).

30 The autoclaves were charged with liquid monomer and initiator (AIBN), subsequently cooled with liquid nitrogen and purged several times by placing under a vacuum and by purging with nitrogen via a stainless steel pipe under a high vacuum. The technique of freezing/thawing cycles was used to remove oxygen from the liquid phase. Subsequently, the desired amount of TFE was condensed in the autoclave.

The polymerization reactions were carried out at various temperatures (60-75°C ) under the pressure suitable for TFE to 10-12% conversion of the monomers.

5 After the polymerization, the unreacted TFE was  
purged and the comonomers were first recovered by  
distillation and subsequently the copolymer was  
dried under vacuum ( $10^{-2}$  mmHg at 50-60°C) to  
constant weight. The reactivity ratios  $r_i$  of the  
10 comonomers were calculated by the Tidwell and  
Mortimer methods and TFE proved to be more  
reactive than the monomer FA1 ( $r_{FA1} = 0.41$  and  $r_{TFE}$   
= 2.47).

b) 4,5,5-trifluoropent-4-en-1-ol (FA2)

15 The bulk copolymerization of TFE with 4,5,5-tri-  
fluoropent-4-en-1-ol was carried out by a  
batchwise process in 30 and 50 cm<sup>3</sup> stainless steel  
autoclaves equipped with a magnetic stirrer, a  
safety valve, an accurate manometer ( $\pm 0.01$  MPa)  
20 and a thermometer ( $\pm 0.2^\circ\text{C}$ ).

The autoclaves were charged with liquid monomer  
and initiator (AIBN), subsequently cooled with  
liquid nitrogen and purged several times by  
placing under a vacuum and by purging with  
25 nitrogen via a stainless steel pipe under a high  
vacuum. The technique of freezing/thawing cycles  
was used to remove oxygen from the liquid phase.  
Subsequently, the desired amount of TFE was  
condensed in the autoclave.

30 The polymerization reactions were carried out at  
various temperatures (60-75°C ) under the pressure  
suitable for TFE to 10-12% conversion of the  
monomers.

After the polymerization, the unreacted TFE was  
35 purged and the comonomers were first recovered by  
distillation and subsequently the copolymer was  
dried under vacuum ( $10^{-2}$  mmHg at 50-60°C) to  
constant weight. The reactivity ratios  $r_i$  of the  
comonomers were calculated by the Tidwell and

Mortimer methods and TFE proved to be more reactive than the monomer FA2 ( $r_{FA2} = 0.45$  and  $r_{TFE} = 1.57$ ).

Example 8

5           Emulsion       (ternary)       copolymerization       of  
4,5,5-trifluoropent-4-en-1-ol with tetrafluoroethylene  
(TFE) and propylene

10           A 250 cm<sup>3</sup> stainless steel autoclave (Buchi,  
Switzerland) was used as container for the  
terpolymerization of TFE with propylene and  
4,5,5-trifluoropent-4-en-1-ol in a batchwise operation.  
The reactor was equipped with a cooling/heating jacket,  
with a paddle magnetic stirrer, with a pressure gauge,  
with a safety valve and with a measuring unit  
15 (monitoring of the pressure, stirring and temperature).  
The components were prepared separately (solutions A  
and B). The TFE/propylene monomer ratio was maintained  
at 80/20 mol% (total amount of monomers: 17.7 g) but  
the initial percentage of 4,5,5-trifluoropent-4-en-1-ol  
20 was varied within the range from 1.7 to 14.1 mol%.

25           The other components of all the compositions  
were as follows: H<sub>2</sub>O (125 g); t-butanol<sup>a</sup> (36.8 g/l);  
Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O<sup>b</sup>/NaOH<sup>b</sup> = 8/0.8 g/l; C<sub>7</sub>F<sub>15</sub>COONH<sub>4</sub>(FC-143)<sup>b</sup>  
(10.10 g/l). The redox system comprised (mmol/l):  
t-butyl peroxobenzoate (TBPB)<sup>a</sup> (10.30); FeSO<sub>4</sub>·7H<sub>2</sub>O<sup>b</sup>  
(0.22); EDTA 2Na·2H<sub>2</sub>O<sup>b</sup> (0.22); HOCH<sub>2</sub>SO<sub>2</sub>Na·2H<sub>2</sub>O<sup>b</sup> (12.70),  
where "a" indicates the components of the solution A  
and "b" those of the solution B.

30           The autoclave was closed and the two solutions  
were purged by a flow of nitrogen. Subsequently, the  
reactor was charged with the two solutions under an  
inert atmosphere. The amounts of TFE and of propylene  
required in order to maintain their initial molar ratio  
at 80/20 and the initial pressure at 1.55 MPa for each  
35 experiment were introduced into the container while  
stirring at 800-850 rev/min. The temperature of the  
experiments was maintained by a thermostat at  
25 ± 0.2°C. At the end of the copolymerization, the  
latex was coagulated by cooling the total product

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### Example 9

5 acetate (FAC) with vinylidene fluoride (VDF)

for a total vol of 8 cm<sup>3</sup>). After having introduced the initiator (0.05 mol% to the mixture of monomers) and the FAc, the tube was connected to a pipe for placing under vacuum and rinsed several times by placing under vacuum and by rinsing with helium. After 5 freezing/thawing cycles, the vinylidene fluoride was trapped under vacuum in the tube frozen with liquid nitrogen, after the reduction in pressure in a calibrated pressure intermediate metal container. The required amount of vinylidene fluoride (0.50-1.00 g) introduced into the tube was obtained by a relative fall in the pressure in this pressure-reducing container fed initially via a 300 g cylinder of vinylidene fluoride.

25 nitrogen, was sealed and placed in the chamber of an oven incorporating agitation at 120°C for 17 hours.

30 to constant weight.

35 recorded on Bruker AC-200 or Bruker AC-250 instruments using deuterated acetone or dimethylformamide as solvents and tetramethylsilane (TMS) or  $\text{CFCl}_3$  as internal references, respectively.

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heptane. The solid polymer was dried at 60-70°C under vacuum to constant weight.

4.36 g of a white solid were obtained (yield of approximately 18%).

5           This powder was soluble in acetone, acetonitrile, DMF and THF at ambient temperature but it was insoluble in cyclohexane, hexane, heptane and toluene, even on heating slightly (40°C).

Example 11

10           Crosslinking of poly(vinylidene fluoride) (PVDF) carrying mercapto functional side groups

a) Hydrolysis of the VDF/FSAc copolymer

15           10 ml of methanol and 10 ml of acetone were introduced into a three-necked round-bottomed flask equipped with a reflux condenser and an inlet for a flow of nitrogen. After degassing and after sparging this mixture with nitrogen, 0.18 g (2.77 mmol) of potassium cyanide and 3.2 g (approximately 1.28 mmol) of VDF/FSAc copolymer were added.

20           The mixture was stirred at ambient temperature for 15 h. After the reaction, the hydrolysed copolymer was precipitated from water. 1.79 g of PVDF carrying mercapto functional side groups were obtained.

25           b) Crosslinking proper

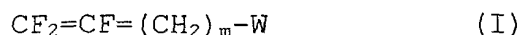
30           A small tube made of borosilicate comprising 1.13 g (0.45 mmol) of PVDF carrying mercapto functional side groups, 1.30 g (15.8 mmol) of 1,5-hexadiene, 0.055 g (0.31 mmol) of t-butyl peroxy-pivalate and 5.04 g of acetonitrile was degassed and purged with helium. Subsequently, after 5 freezing/thawing cycles, it was sealed under vacuum and introduced into an oven with stirring. The tube was stirred for 5 h at 75°C. After the reaction, a beige precipitate appeared at the bottom of the tube. After freezing in liquid nitrogen, the tube was opened. The solvent and the excess 1,5-hexadiene were evaporated and

35

the brown solid was dried at 70°C under vacuum for 3 h (1.43 g were obtained). The product was insoluble in polar and nonpolar solvents.

## CLAIMS

1. Compound corresponding to the formula I



chosen from the compounds in which

- 5 (i) m has the value 1, 2 or 3 and

W represents a  $\begin{array}{c} \text{P}-\text{R}_1 \\ | \\ \text{R}_2 \end{array}$  group, a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{R}_3 \\ | \\ \text{R}_4 \end{array}$  group or a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{OR}_5 \\ | \\ \text{R}_6 \end{array}$  group,

in which

- 10  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group

- $\text{R}_5$  and  $\text{R}_6$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group, with the proviso that, when  $\text{R}_5$  represents a hydrogen atom,  $\text{R}_6$  is other than a phenyl group when m has the value 1;

- 15 (ii) m has the value 3 and

W represents a  $\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{OR}_7 \\ | \\ \text{OR}_8 \end{array}$  group

in which

- 20  $\text{R}_7$  and  $\text{R}_8$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group;

- (iii) m has the value 1 and

W represents a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group;

- (iv) W represents a Y-Z group chosen from

- 25 (1) a Y-Z group in which

Y represents an oxygen atom and

Z represents a  $\text{CH}_2\text{CH}_2\text{OH}$  group or a  $\text{CH}_2\text{COOH}$  group and

m has the value 1, 2 or 3

- 30 (2) a Y-Z group in which

Y represents an oxygen atom and

Z represents a  $\text{COCH}_3$  group, and

m has the value 1 or 3

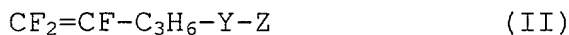
- (3) a Y-Z group in which

- 35 Y represents a sulphur atom and

Z represents a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group or a  $\text{COCH}_3$  group, and

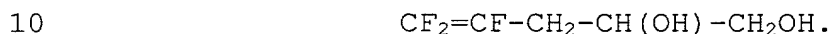
m has the value 3.

2. Compound according to Claim 1, corresponding to the formula II

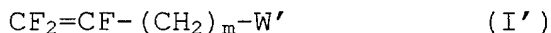


in which Y and Z are as defined in Claim 1.

3. Compound according to Claim 1, corresponding to the formula



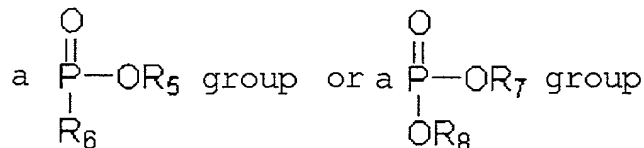
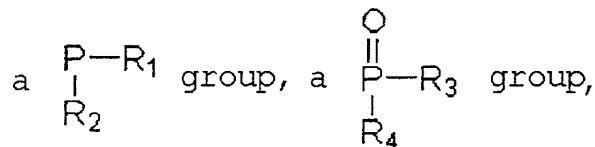
4. Copolymerization process comprising the reaction of a compound corresponding to the formula I'



in which

- m has the value 1, 2 or 3,

W' represents a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group, a  $\text{CH}=\text{CH}_2$  group,



in which

- 20  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$  and  $\text{R}_8$  independently represent a hydrogen atom, a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or an optionally substituted aryl group or

W' represents a Y-Z group chosen from

- (1) a Y-Z group in which

Y represents an oxygen atom and

- 25 Z represents a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group or a  $\text{COCH}_3$  group,

- (2) a Y-Z group in which

Y represents a sulphur atom and

- 30 Z represents a hydrogen atom, a  $\text{CH}_2\text{CH}_2\text{OH}$  group, a  $\text{CH}_2\text{COOH}$  group or a  $\text{COCH}_3$  group,

with a compound corresponding to the formula III

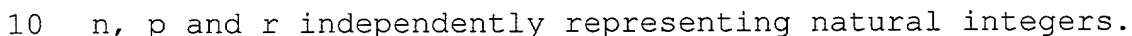


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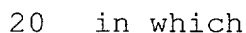
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X independently represents a hydrogen atom or a fluorine atom,

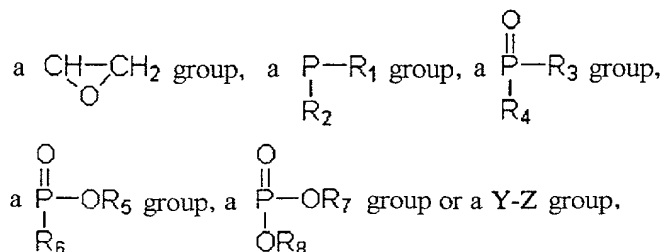
5 5. Copolymerization process according to Claim 4,  
in which Y represents an oxygen atom, Z represents a  
COCH<sub>3</sub> group and the copolymer obtained corresponds to  
the formula V


$$\left[ \left( \text{CF}_2 - \text{CX}_2 \right)_n \left[ \text{CF}_2 - \underset{\begin{array}{c} | \\ (\text{CH}_2)_m \\ | \\ \text{S} \\ | \\ \text{COCH}_3 \end{array}}{\text{CF}} \right]_p \right]_r \quad (\text{VI})$$

7. Copolymerization process comprising the reaction of a compound corresponding to the formula I'



W' represents a  $\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group, a  $\text{CH}=\text{CH}_2$  group,



in which

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  independently represent a hydrogen atom, a  $C_1$ - $C_{20}$  alkyl group or an optionally substituted aryl group

5 Y represents an oxygen atom or a sulphur atom and

Z represents a hydrogen atom, a  $CH_2CH_2OH$  group, a  $CH_2COOH$  group or a  $COCH_3$  group,

with a compound corresponding to the formula III

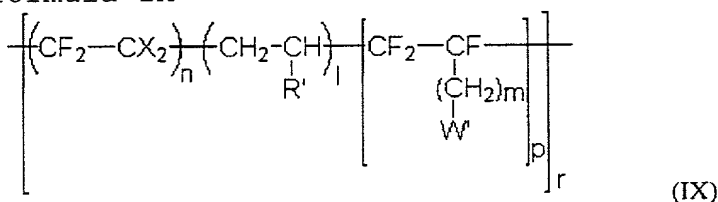


10 in which

X independently represents a hydrogen atom or a fluorine atom

and with an olefinic compound of formula  $CH_2=CH-R'$  in which  $R'$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl group,

15 so as to obtain a copolymer corresponding to the general formula IX



in which

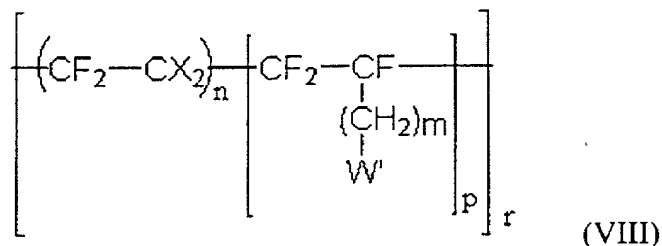
20 1, n, p and r independently represent natural integers.

8. Process according to Claim 7, in which Z represents a  $CH_2CH_2OH$  group, a  $CH_2COOH$  group or a  $COCH_3$  group.

9. Process according to Claim 7 or 8, in which the  
25 olefinic compound is propylene.

10. Use of the process according to any one of Claims 4 to 9 in forming fluoroelastomers.

11. Copolymer corresponding to the general formula VIII



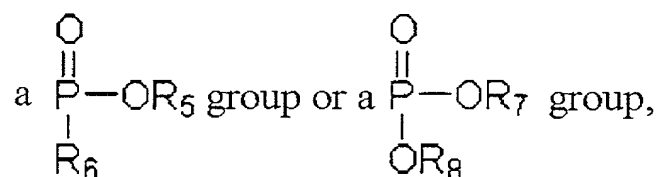
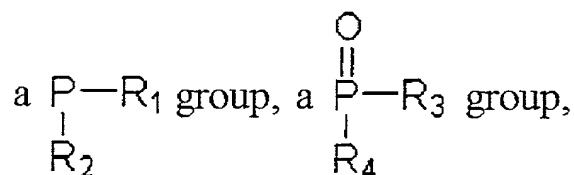
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

5 n, p and r independently represent natural integers, and

W' represents a CH(OH)CH<sub>2</sub>OH group, a CH=CH<sub>2</sub> group,



in which

10 R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> independently represent a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group or an optionally substituted aryl group or

W' represents a Y-Z group chosen from

(1) a Y-Z group in which

15 Y represents an oxygen atom and

Z represents a CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group or a COCH<sub>3</sub> group,

(2) a Y-Z group in which

Y represents a sulphur atom and

20 Z represents a hydrogen atom, a CH<sub>2</sub>CH<sub>2</sub>OH group, a CH<sub>2</sub>COOH group or a COCH<sub>3</sub> group.

12. Copolymer according to Claim 11, in which Y represents an oxygen atom and Z represents a COCH<sub>3</sub> group.

25 13. Copolymer according to Claim 11, in which Y represents a sulphur atom and Z represents a COCH<sub>3</sub> group.

14. Copolymer corresponding to the general formula IX





ABSTRACT

Functional trifluorovinyl monomers and their  
copolymerization with fluoroolefins

Functional trifluorovinyl monomers, process for the copolymerization of trifluorovinyl monomers with fluoroolefins and use of these trifluorovinyl monomers in forming fluoroelastomers.

Copolymers resulting from this copolymerization process and process for crosslinking these copolymers.

No figure.

05856774-073404

398135

COMBINED DECLARATION AND POWER OF ATTORNEY

Attorney Docket No.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled Functional trifluorovinyl monomers and their copolymerization with fluoroolefins the specification of which

(check one) ☐ is attached hereto.

☒ was filed on November 22, 1999 as

Application Serial No. 09/856,774 and

was amended on \_\_\_\_\_  
(if applicable)

was amended through \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed
<u>98.14931</u>	<u>France</u>	<u>25/11/1998</u>	<input checked="" type="checkbox"/> <input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes No
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes No
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
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I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

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(Application No.) (filing date)

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<u>PCT/EP99/09147</u>	<u>22/11/1999</u>	<u>Pending</u>
(Application Serial No.)	(Filing Date)	(Status)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

598135

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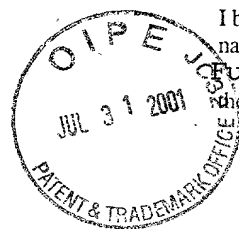
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09856774-03404

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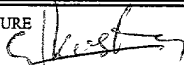
Rudolf E. Hutz, Reg. No. 22,397; Harold Pezzner, Reg. No. 22,112; Richard M. Beck, Reg. No. 22,580; Paul E. Crawford, Reg. No. 24,397; Thomas M. Meshbesh, Reg. No. 25,083; Patricia Smink Rogowski, Reg. No. 33,791; Robert G. McMorrow, Jr., Reg. No. 30,962; Ashley I. Pezzner, Reg. No. 35,646; William E. McShane, Reg. No. 32,707; Mary W. Bourke, Reg. No. 30,982; Gerard M. O'Rourke, Reg. No. 39,794; Allan N. Kutzenco, Reg. No. 38,945; and James M. Olsen, Reg. No. 40,408 all of P.O. Box 2207, Wilmington, Delaware 19899-2007 my attorneys with full power of substitution and revocation.

Send Correspondence To: <b>Connolly, Bove, Lodge &amp; Hutz, LLP</b> P.O. Box 2207 Wilmington, Delaware 19899-2207		Direct Telephone Calls To: (302) 658-9141	
FULL NAME OF SOLE OR FIRST INVENTOR <b>1-00 PETROVA, Petya</b>		INVENTOR'S SIGNATURE 	
RESIDENCE <b>Quartier Dame Grouev, bat. 8, Appart. 22, 8800 SLIVEN (Bulgaria)</b>		DATE <b>July 19, 2001</b> CITIZENSHIP <b>Bulgaria</b>	
POST OFFICE ADDRESS <b>"same as above"</b> <span style="float: right;">BGT</span>			
FULL NAME OF SECOND JOINT INVENTOR		INVENTOR'S SIGNATURE	
RESIDENCE		DATE	
POST OFFICE ADDRESS			
FULL NAME OF THIRD JOINT INVENTOR		INVENTOR'S SIGNATURE	
RESIDENCE		DATE	
POST OFFICE ADDRESS			
FULL NAME OF FOURTH JOINT INVENTOR		INVENTOR'S SIGNATURE	
RESIDENCE		DATE	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH JOINT INVENTOR		INVENTOR'S SIGNATURE	
RESIDENCE		DATE	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH JOINT INVENTOR			
RESIDENCE			
POST OFFICE ADDRESS			

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FULL NAME OF SOLE OR FIRST INVENTOR <u>KOSTOV, Georges</u>		INVENTOR'S SIGNATURE 	
RESIDENCE <u>Komplex Slaveykore, Bat. 38, Appart. 11</u> <u>8010 BOURGAS (Bulgaria) BGX</u>		DATE <u>July 2, 2001</u> CITIZENSHIP <u>Bulgaria</u>	
POST OFFICE ADDRESS <u>"same as above"</u>			
FULL NAME OF SECOND JOINT INVENTOR		INVENTOR'S SIGNATURE	
RESIDENCE		DATE	
CITIZENSHIP			
POST OFFICE ADDRESS			
FULL NAME OF THIRD JOINT INVENTOR		INVENTOR'S SIGNATURE	
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RESIDENCE		DATE	
CITIZENSHIP			
POST OFFICE ADDRESS			
FULL NAME OF SIXTH JOINT INVENTOR			
RESIDENCE			
POST OFFICE ADDRESS			

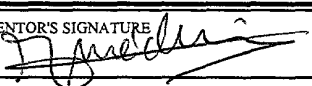

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FULL NAME OF SOLE OR FIRST INVENTOR <b>AMEDURI, Bruno</b>		INVENTOR'S SIGNATURE 	DATE <b>May 10<sup>th</sup> 2001</b>
RESIDENCE <b>Rue de la Treille Muscate, 28, F-34090 MONTPELLIER</b>		CITIZENSHIP <b>France</b>	
POST OFFICE ADDRESS <b>"same as above"</b> <b>FRX (France)</b>			
FULL NAME OF SECOND JOINT INVENTOR <b>BOUTEVIN, Bernard</b>		INVENTOR'S SIGNATURE 	DATE <b>May 10<sup>th</sup> 2001</b>
RESIDENCE <b>Les Terres Blanches, 1, rue Anselme Mathieu</b>		CITIZENSHIP <b>France</b>	
POST OFFICE ADDRESS <b>F-34090 MONTPELLIER (France) FRX</b> <b>"same as above"</b>			
FULL NAME OF THIRD JOINT INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FOURTH JOINT INVENTOR		INVENTOR'S SIGNATURE	DATE
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RESIDENCE			
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